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DEGRADATION OF SLUDGES FROM HEAVY CRUDES IN CONTAINED REACTORS

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Maintenance and Monitoring of Laboratory Reactors
[Part of the Program of the Federal Panel on Energy R&D (PERD)]

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EXECUTIVE SUMMARY

Three bench scale bioreactors for oily sludge degradation were maintained and monitored over a 14 month period. One reactor contained sludge from refining light conventional oil and the other two contained heavy oil sludge. Microbial numbers in the bioreactors remained high and the organisms were active over the period of study. The reactor containing sludge from conventional oil refining, maintained a temperature two degrees above ambient while the reactors containing heavy oil sludge maintained ambient temperatures.

Significant levels of carbon dioxide were released from all three reactors but evolution was highest from the reactor containing sludge from conventional oil refining. One reactor containing heavy oil sludge appeared to release a component which inhibited algal growth.

The oil contents in all three reactors decreased by 70% over the period of operation and correlate with sustained microbial numbers, elevated temperatures and carbon dioxide evolution indicating biodegradation. Polyaromatic hydrocarbons did not accumulate in the leachate from the reactors indicating that they also were being degraded.

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SOMMAIRE

Pendant 14 mois, nous avons étudié la dégradtion du pétrole dans les réacteurs fermés. Un réacteur a contenu la vase du pétrol légèr and deux reacteurs ont contenu la vase du pétrole lourd. Les vases ont été absorbées avec le producìt de la tourbe, Oclansorb. Les nombres de microbes dans les réacteurs ont restés elevés pendant l'étude. La température du réacteur contennant la vase du pétrol légèr a resté deux dégres en haut d'ambiant tandis que les températures des réacteurs contenants la vase du pétrole lourde restaiennent égal a l'ambiant.

L'oxide du charbon échappit des réacteurs mais le niveau le plus elevé etait lié avec la vase provenant du pétrole légèr. Il apparait qu'un réacteur contenant la vase du pétrole lourd a évolu un produit volatil qui a abaissé la croissance de l'Algue.

Les contenus huileus des réacteurs ont étés réduits de 70% pendant les 14 mois. La biodégradation de l'huile était indiqué par les nombres éleves des microbes, les température élevées et le niveau de l'oxide du charbon. Les molécules aromatiques polynucleares etaint degradees aussi.

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1.0 OBJECTIVE

To monitor oil degradation in lab scale bioreactors equipped with leachate recycle.

2.0 INTRODUCTION

Following initial success with a field reactor to degrade oil sludge from conventional oil refining, three bench scale reactors were constructed to study degradation of heavy oil sludge (Figure 1) and to compare it with degradation of sludge from conventional oil refining (1). Initial results indicated that in the presence of Oclansorb oil absorbent 33% - 55% of the oil in the reactors was degraded over a six week period (1).

In that study problems were encountered in obtaining accurate, reliable and quantifiable oil recovery from the reactors due to variations in refluxing times for oil extraction and probably sampling variability. It was therefore decided to allow the reactors to run over a longer time period and to monitor over that period with particular attention to standardization of the oil extraction procedure.

3.0 MATERIALS AND METHODS

3.1 Microbial Analysis

Enumeration of microbes in the reactors was performed by the most probable number technique. Replicate samples from each sampling time for each reactor were serially diluted from 10^{-1} to 10^{-12} in tubes of liquid culture medium and incubated for 14 days at ambient temperature. Turbid tubes indicating microbial growth were enumerated. These data were applied to standard probability tables published for this technique to estimate the number of bacteria per gram of solid material in the reactor (2).

Complex medium used to test for heterotrophic growth contained per litre:

K_2HPO_4	10.0 g
NaH_2PO_4	5.0 g
NH_4NO_3	2.0 g
$MgSO_4.2H_2O$	0.2 g
$CACl_2.2H_2O$	0.001 g

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$FeSO_4.7H_2O$	0.001 g
Yeast extract	0.4 g
Nutrient broth	0.4 g
Distilled water	1 L

Minimal medium for enumeration of oil degrading organisms contained:

$K_2HPO_4.3H_2O$	13.1 g
$NaH_2PO_4.H_2O$	5.75 g
NH_4NO_3	2.0 g
$MgSO_4.7H_2O$	0.315 g
$CaCl_2.2H_2O$	0.0006 g
$FeSO_4.7H_20$	0.001 g
Distilled water	1 L

Final pH = 6.8

This medium was dispensed 4.5 mL per tube. After the tubes were inoculated, 50 microlitres of Amauligak crude oil or 50 microlitres of toluene containing 15 mg naphthalene were added to each tube of minimal medium. The toluene evaporated within 24 hours leaving crystals of naphthalene floating on the surface of the medium. Organisms which grew on and degraded the oil turned the medium in the tubes turbid and dispersed the oil. Organisms which grew on and degraded the naphthalene turned the medium in the tubes turbid and caused disappearance of the naphthalene crystals. In control tubes without microbes, the naphthalene crystals did not disappear.

3.2 PAH Analysis

Analysis for the presence of polyaromatic hydrocarbons (PAH's) in the leachate water was performed by Core Laboratories, Calgary, Alberta. PAH's were analysed by the EPA 625 method after extraction with dichloromethane from 250 mL water samples. Analysis was on an HP 5890 gas chromatograph and an HP 5970 mass spectrometer.

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3.3 Extracted Oil

Samples (50 - 100 gram) of Oclansorb/oil matrix were removed from the reactors for oil extraction and analysis. Oil extraction was performed for six hours by the technique of Dean and Stark (Appendix 1) using hot dichloromethane. The Oclansorb matrix was dried and weighed after extraction. The dichloromethane was removed by rotary evaporation and the residual oil was weighed. A 20 mg sample of the extracted oil was dissolved in 1 mL of carbon disulfide and used for gas chromatography to obtain its characteristic fingerprint.

Gas chromatography was performed with a Perkin Elmer Sigma 2000 gas chromatograph equipped with an SPB-5 fused silica capillary column (30 m x 0.32 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 30 mL/min. The purge gas flow was 3 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 70 degrees for ten minutes, then increase the temperature by 10 degrees per minute up to 100 degrees, followed by a 3 degree per minute increase up to 300 degrees. The temperature was maintained at 300 degrees for 30 minutes. The output of the resulting data was on an HP3390A integrator with chart speed set at 0.4 cm/min. A one microlitre sample was use for injection.

4.0 RESULTS

4.1 History of Reactors

Reactors 1, 2 and 3 were established at NHRC in January 1989. Reactor 1 contained tank bottoms sludge from Husky Oil's conventional oil refinery at Prince George, B.C. treated with 0.075 moles of potassium permanganate/Kg sludge. Reactor 2 contained heavy oil desalter sludge #1 from Husky Oil's Lloydminster refinery treated with 0.075 moles potassium permanganate/Kg sludge. Reactor 3 contained heavy oil desalter sludge #2 from Husky Oil's Lloydminster refinery treated with 0.075 moles potassium with permanganate/Kg sludge. The sludges were treated with permanganate before microbial exposure to effect preoxidation of aromatic species in the oil.

After a six week period, preliminary results had indicated degradation primarily of the saturate fraction of the oil in all three reactors. Reactor 1 had 34% oil loss, Reactor 2 had 55% oil loss and Reactor 3 had 38% oil loss. It was suggested that allowing the reactors to run fro a longer period would allow improved quantization of the results. It was also concluded that the level of

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permanganate used to pretreat the oily sludge was insufficient to effect preoxidation before microbial attack.

4.2 Microbial Numbers

The numbers of oil degrading microbes remained at the same levels as reported previously in the 10^8/g - 10^9/g range (Table 1). Reactor 1, containing tank bottoms sludge from conventional oil refining at Prince George, consistently contained slightly higher numbers of oil degraders than Reactors 2 and 3 containing desalter sludges #1 and #2 from heavy oil refining at Lloydminster. At 14 months operation the frequency of organisms capable of degrading naphthalene were in the 10^3/g range representing 1.86 x 10-4 %, 1.5 x 10^{-2} % and 1 x 10^{-4} % of the oil degrading organisms in Reactors 1, 2 and 3, respectively (Table 1). However, organisms from reactors 2 and 3, while growing on Amauligak oil, produced red, purple and brown colored water-soluble substances somewhat similar to colored metabolites from microbial degradation of polyaromatics (3, 12). The organisms capable of performing this task were present at the 10^5/g - 10^6/g range in Reactors 2 and 3 and were absent in Reactor 1 based on MPN calculations of the frequency of pigment production in tubes used to enumerate growth on Amauligak oil.

Comparison of the GC spectra of the recovered Amauligak oil from these tubes with that recovered from those tubes inoculated with organisms from Reactor 1, showed that the saturate alkane peaks were removed from all samples. However, additional specific peaks, supposedly aromatics, were removed from the oil inoculated with the organisms growing in Reactors 2 (Figure 2) and Reactor 3. Such peaks were not removed from the tubes inoculated with organisms from Reactor 1.

4.3 Temperature

The temperature of the reactors fluctuated somewhat with the ambient temperature. However, Reactor 1, which contained the sludge from conventional oil, consistently had the highest temperature, approximately two degrees above ambient (Table 2). Reactors 2 and 3, containing heavy oil sludge, generally were a fraction of a degree above or below ambient temperature.

4.4 Carbon Dioxide Evolution

Evolution of carbon dioxide gas was measured intermittently. The highest levels of this gas were present in Reactor 1. Generally, evolved carbon dioxide in Reactors 2 and 3, containing heavy oil

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sludge, was at 50% or less the level in Reactor 1 (Table 3). The level of evolved carbon dioxide increased dramatically in all reactors after they were recharged with fresh nitrogen and phosphorus sources at seven months. However, after nutrient recharge at fourteen months operation, the level of evolved carbon dioxide increased by 16% in Reactor 1 only (Table 3).

The gases evolved from Reactors 1 and 2 allowed growth of an algal population in the water traps (Figure 3). The effluent gas from Reactor 3 did not permit such growth even when Reactor 3 trap was inoculated with algae from Reactor 2 trap. This suggests evolution of volatiles from Reactor 3 inhibitory to algal growth.

4.5 PAH Analysis

The aqueous leachate from the reactors contained bi- and tricyclic hydrocarbon species at less than 3 microgram/L level, the detection limit (Table 4).

4.6 Hydrocarbon Content

Total hydrocarbon content of the reactors decreased over the year. After six weeks operation, the reactors had lost 33% of the oil in Reactor 1, 55% in Reactor 2 and 38% in Reactor 3 (Table 5) (1). By seven months operation calculated losses were 30% - 37% in Reactor 1 and 27% to 35% in Reactor 2. Oil content of Reactor 3 varied from a gain of 19% to a loss of 19% (Table 5). By fourteen months oil losses were 73% in Reactor 1, 78% in Reactor 2 and 64% in Reactor 3.

Gas chromatograms of the oil recovered from the three reactors over the year's operation revealed the degradation progress of the oil. Oil from Reactor 1 showed losses in the > C-35 saturated fraction of the oil (Figure 4). There was also fluctuation in the relative intensities of the lower molecular weight alkane peaks (Figure 4).

Gas chromatograms of the recovered heavy oil revealed losses of original peaks at 45 and 64 minutes of the chromatogram over the year (Figure 5). The bulk of complex material in heavy oil sludge was not resolvable by gas chromatography and eluted as an unchanged hump at 32 - 56 minutes and 77 - 93 minutes of the chromatograms (Figure 5).

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5.0 DISCUSSION

5.1 Microbial Numbers

The total number of viable microbes remained high in all three reactors over the year's operation. The relative constancy of the number of oil degraders indicates a sustained population capable of degrading the oil and probably reflects the ongoing oil degradation in the reactors. The greater number of oil degraders present in Reactor 1 may reflect an increased amount of oil degradation taking place in that vessel. It might also just represent the number of organisms capable of degrading the alkanes present in the light conventional Amauligak crude oil used to assess oil degradation since Reactor 1 contains tank bottoms high in alkanes from conventional oil refining.

The high numbers of oil degraders growing on the different species of sludge present in the three reactors, suggested adaptation and selection of organisms capable of degrading the hydrocarbon species predominant in each particular sludge. Organisms capable of degrading aromatics are different from those capable of degrading alkanes (3) and so it was expected that aromatic degraders would proliferate in reactors degrading the Lloydminster heavy oil sludge containing complex aromatic structures (10) (Figure 6). Organisms capable of degrading naphthalene, the bicyclic compound used as a typical aromatic substrate species, did constitute a larger percentage of the organisms present in Reactor 2 which reported a slightly higher oil loss than Reactor 3. However, the numbers of naphthalene degraders were low in all three reactors after a year's operation.

It has been suggested that lack of growth on oil constituents may be due to failure to solubilize and transport the substrate into the microbial cell rather than to an inability of the organism to degrade the material (4,9). This is an unlikely explanation for low numbers of naphthalene degraders in the present study as in another study high numbers of naphthalene degrading organisms have been identified among species growing on Lloydminster heavy oil sludge (unreported results). However, naphthalene may not have been a representative aromatic substrate at 14 months in the current study. It is possible that naphthalene-like compounds have been removed from the oil either by microbial action or air stripping by 14 months and the population has selected organisms capable of degrading higher order ring compounds and having a reduced affinity for naphthalene. An isolate of *Mycobacterium* was reported to degrade the four ring PAH, pyrene, faster than the three ring PAH, phenanthrene or the two ring PAH, naphthalene (5). It is also possible that these organisms can initiate an attack on naphthalene but are unable to metabolize it thoroughly for growth. It has been found that a mixed population of seven

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organisms is required to degrade fluoranthene and other PAH's and use the products for growth (6) and a mixture of 6 organisms is required for complete degradation of dichlorophenol (7).

In any case, since the complex heavy oil in Reactors 2 and 3 are being degraded, microbes capable of performing this task must be present. Production of colored products by organisms present in these reactors when grown on Amauligak crude in a dilution series suggests that organisms responsible for biodegradation of the heavy oil sludge may be producing colorful breakdown products of polyaromatic compounds.

5.2 Temperature

Although the temperature of the reactors fluctuated somewhat with the ambient temperature, Reactor 1 maintained the highest overall temperature. This increased temperature should be indicative of increased microbial activity on the oil in this reactor and agrees with the highest numbers of oil degraders present in this reactor. Lower temperature increases in Reactors 2 and 3 should be reflective of less microbial activity. This correlates with lower levels of carbon dioxide released from Reactors 2 and 3.

5.3 Carbon Dioxide Evolution

Increased levels of carbon dioxide in the headspace gases of the reactors over the levels in the ambient air also indicate ongoing microbial activity in the reactors. Reactor 1 consistently contained the highest carbon dioxide levels in the headspace gas. This concurs with increased temperature and increased numbers of oil degrading bacteria and further indicates increased oil degradation in this vessel. Reactor 1 contains sludge from conventional oil refining which consists primarily of saturate alkane material which is easier to degrade than heavy oil which is rich in multi- nuclear aromatic residues.

A further increase in carbon dioxide evolution on recharging the vessels with nitrogen and phosphorus at seven months indicates that these nutrients may have been limiting at that time. A lesser increase at 12 months, especially in reactors 2 and 3 containing the heavy oil sludge, suggests that at this point the residual oil may consist of the more recalcitrant fraction. Some polyaromatic compounds are not completely degraded to carbon dioxide and water but accumulate in and color the water fraction (3). This has not been observed in the present study as Oclansorb released a brown pigment into the water fraction obscuring any other colors possibly accumulating from incomplete metabolism of polyaromatics.

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Sufficient carbon dioxide was released from Reactors 1 and 2 to support an algal bloom in the water traps. Since the level of carbon dioxide in Reactor 3 was similar to that in Reactor 2, lack of algal growth in the trap of Reactor 3 may be due to emission of some material from this reactor toxic to the algae or to other microorganisms in the trap antagonistic to the algae. No attempts were made to identify components in the effluent gases from Reactor 3, but previous analyses of the water traps from all reactors did not reveal any soluble organic species including PAH's or alcohols released from this reactor (1).

5.4 PAH Analysis

The overall concentration of PAH's in the leachate was low. It is difficult to quantify this material because of volume changes in the water fraction over the course of the study due to evaporation and replacement. Concentrations of PAH's are generally in the order of tens to hundreds of milligrams per kilogram of oily sludge and solubilities are in the order of 0.004 to 30 mg/L of water (11). Since PAH's are not believed to be readily degraded, they should accumulate over time. Lack of their presence in the reactor leachates indicates they are being biodegraded. This agrees with observations made in the bioreactors previously (1).

5.5 Hydrocarbon Content

Calculations of oil losses from the reactors indicated 64% - 78% of the oil was lost over the year. This is more reasonable than the 34% - 55% oil lost over a six week period reported previously (1). The current oil loss is reflected by sustained oil degrading populations, by carbon dioxide evolution and temperature increases in the reactors.

Surprisingly, no peaks in the chromatograms representing specific lower molecular weight alkanes were preferentially totally lost over the period of operation from Reactor 1 which contained waxy sludge from conventional oil refining. It is generally believed that the smaller molecules will be degraded first leaving the larger molecules behind. However, since the oil is absorbed to the Oclansorb, any species of alkane component may not necessarily be available to the degrading microbes all at one time. However, the relative intensities of certain peaks changed over the period of study indicating degradation.

Loss of specific peaks in the chromatograms of the degrading oil were observed in the recovered oil from Reactors 2 and 3 containing heavy oil sludge. These may have been alkane molecules.

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Unlike the sludge in Reactor 1, the material in Reactors 2 and 3 is low in alkanes which may fractionate to the Oclansorb surface more readily than heavy components. These may water extract more readily making them more available for biodegradation. There was no evidence of production of alkane molecules as a consequence of heavy oil was degradation in Reactors 2 and 3. Degradation of polycyclic molecules usually produces complex intermediates and does not lead to generation of simple alkane molecules (5,6,7,8) (Figure 7).

6.0 CONCLUSIONS

1. Oil degradation proceeded in lab scale reactors over a 14 month period as measured by microbial numbers, heat and carbon dioxide generation and reduction of oil content.

2. There was no difference in the level of naphthalene degraders present on sludge from heavy oil operations and sludge from conventional oil refining. However, naphthalene degraders were more prominent as a percentage of the population degrading heavy oil sludge.

3. Greater levels of heat, carbon dioxide and numbers of oil degrading microbes were associated with the sludge from conventional oil refining and probably reflects the greater degradability of this material.

4. For the sludge from conventional oil refining, chromatograms of the oil recovered after biotreatment showed loss of higher molecular weight alkane species (> C-35) and some fluctuation of the relative intensities of the lower molecular weight alkane peaks (< C-35).

5. For heavy oil sludge, chromatograms of the oil recovered from biotreatment showed loss of the few peaks resolvable by gas chromatography.

6. PAH's did not accumulate in the leachate waters indicating that they were being biodegraded.

7. Volatiles from one heavy oil sludge reactor appeared to establish conditions inhibitory to algae growth in the effluent gas water trap on the reactor.

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8.0 TABLES

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Table 1:

SAMPLING PERIOD	MICROBES / g MATRIX		
	(HETEROTROPHS*)	(OIL DEGRADERS)	(AROMATIC DEGRADERS)
Reactor 1			
7 months	1.86×10^8	1.50×10^9	-
7.5 months	3.00×10^7	1.83×10^9	-
8 months	8.30×10^8	3.00×10^9	-
14 months	-	$>4.6 \times 10^9$	8.60×10^3
Reactor 2			
7 months	8.60×10^8	1.86×10^8	-
7.5 months	1.86×10^8	1.96×10^8	-
8 months	1.86×10^8	1.86×10^8	-
14 months	-	3.00×10^7	4.60×10^3
Reactor 3			
7 months	1.86×10^8	1.86×10^8	-
7.5 months	1.86×10^8	1.86×10^8	-
8 months	1.50×10^8	1.86×10^8	-
14 months	-	4.60×10^9	4.60×10^3

* Decreased numbers of heterotrophs relative to oil degraders in the samples may be attributed to growth inhibition by the complex carbon sources of nutrient broth and yeast extract in the medium used to enumerate heterotrophs. Inhibition of soil microorganisms by rich complex medium has been noted previously (12).

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Table 2: Temperatures in the Reactors

REACTOR	TEMPERATURE (Degrees C) RUN PERIOD	
	7 months	14 months
REACTOR 1	22.8	21.4
REACTOR 2	21.6	19.0
REACTOR 3	20.5	21.0
AMBIENT CONTROL	20.8	19.0

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Table 3: Carbon Dioxide Gas Evolution in the Reactors

OPERATING PERIOD	CARBON DIOXIDE CONTENT OF HEADSPACE GAS (mg/kg)			
	REACTOR 1	REACTOR 2	REACTOR 3	SOURCE AIR
7 months	1040	670	670	480
1 week later*	4430	2120	1610	460
14 months	1970	720	810	ND+
1 week later*	2280	660	740	490

* The reactors were recharged with nitrogen and phosphorus nutrients 5 - 7 days before samples were taken for analysis.

\+ ND = not determined

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Table 4: Water Analyses

COMPONENT	CONCENTRATION (microgram/L)*		
	REACTOR 1	REACTOR 2	REACTOR 3
Naphthalene	<3	<3	<3
Acenaphthylene	<3	<3	<3
Acenaphthene	<3	<3	<3
Fluorene	<3	<3	<3
Phenanthrene	<3	<3	<3
Anthracene	<3	<3	<3
Pyrene	<3	<3	<3
Benzo(a)anthracene	<3	<3	<3
Chrysene	<3	<3	<3
Benzo(b)fluoranthene	<3	<3	<3
Benzo(k)fluoranthene	<3	<3	<3
Benzo(a)pyrene	<3	<3	<3
Indeno(1,2,3-cd)pyrene	<3	<3	<3
Dibenzo(a,h)anthracene	<3	<3	<3
Benzo(g,h,i)perylene	<3	<3	<3

* A detection limit of 3 microgram/L was used based on a water sample of 250 mL.

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Table 5: Oil Loss in the Reactors

SAMPLING TIME	OIL CONTENT			
	Oil + Solid (g)	Oil (g)	% Oil content	% Oil loss
Reactor 1				
0	18.2	2.31	12.7	0
5 Weeks	11.8	1.12	9.5	25
6 Weeks	21.4	1.81	8.5	33
7 Months (#1)*	19.5	1.71	8.8	30
(#2)	9.9	0.79	8.0	37
14 Months	25.1	0.86	3.4	73
Reactor 2				
0	13.62	1.99	14.6	0
6 Weeks	21.76	1.42	6.5	55
7 Months (#1)*	22.38	2.37	10.6	27
(#2)	9.79	0.92	9.4	35
14 Months	31.09	0.98	3.2	78
Reactor 3				
0	19.17	1.70	8.9	0
6 Weeks	23.82	1.32	5.5	38
7 Months (#1)*	21.68	1.57	7.2	19
(#2)	9.38	0.99	10.6	+19
14 Months	30.95	1.04	3.2	64

* Two different samples were assessed for this sampling point.

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9.0 FIGURES

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Figure 1: A Schematic Drawing of the Reactors

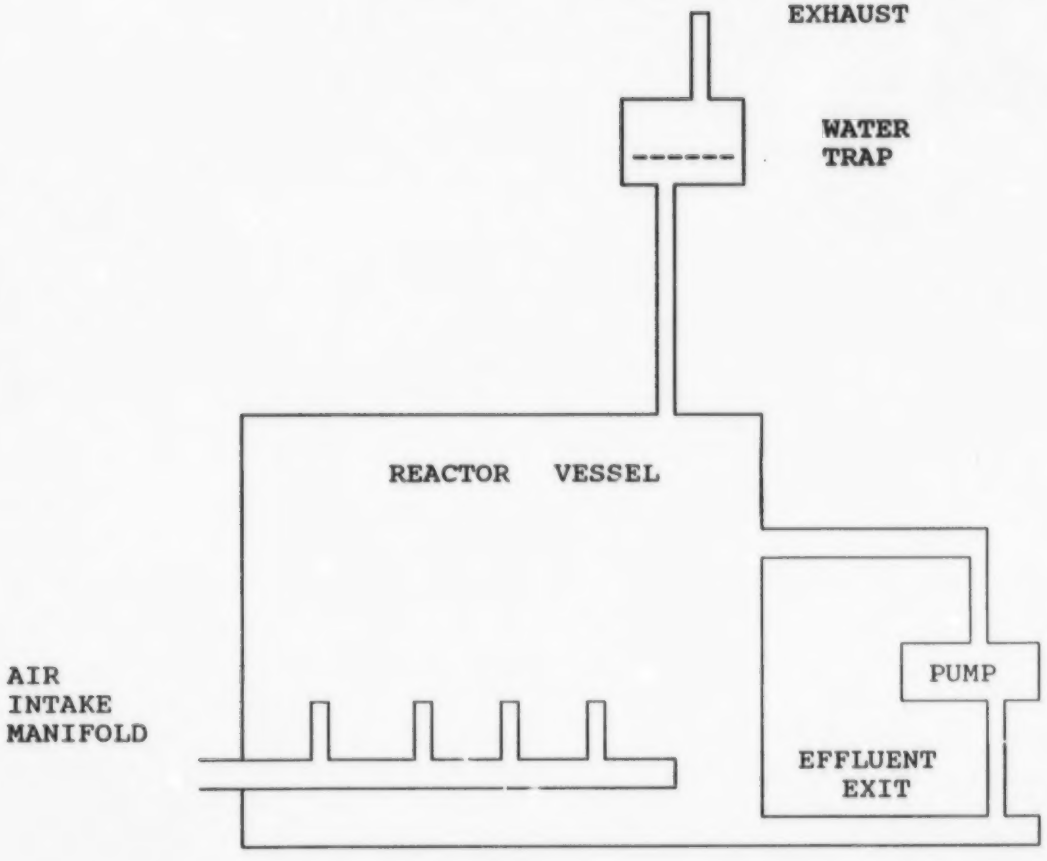

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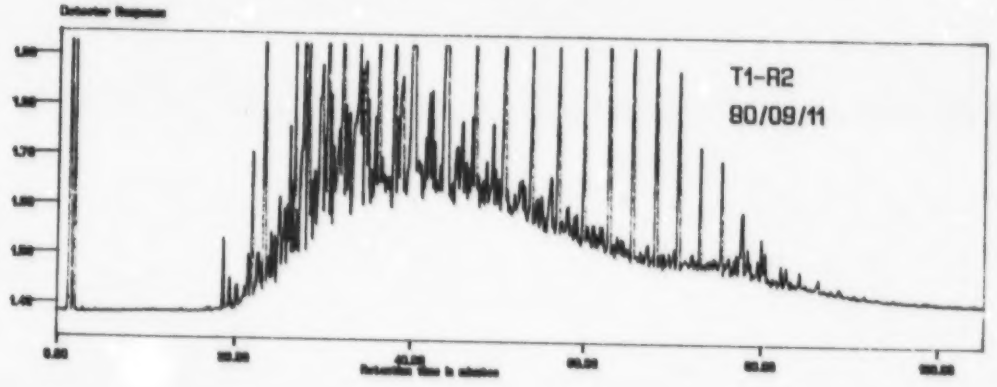
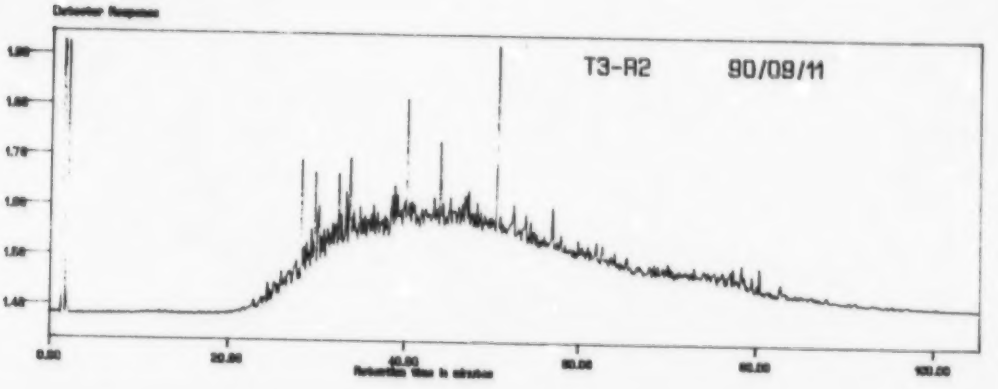
Figure 2: Comparison of the gas chromatograms of Amauligak oil incubated with organisms from reactors 1 and 2

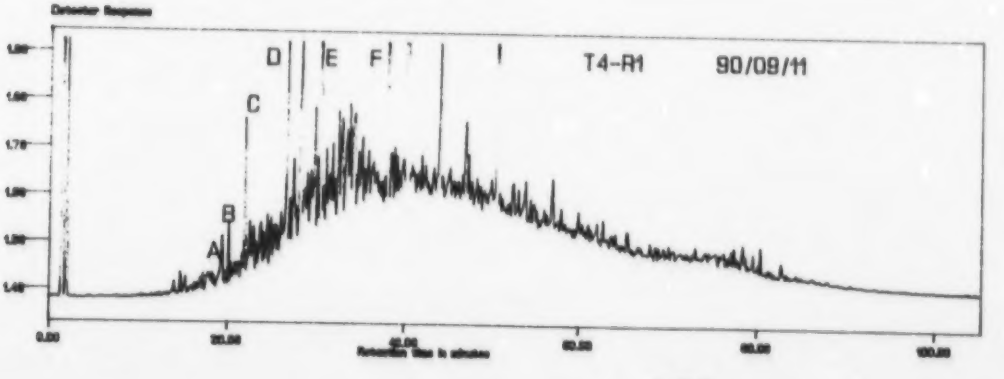
PANEL 1, Control; PANEL 2, + Organisms from Reactor 2; PANEL 3, + Organisms from Reactor 1. The water fraction from samples in PANELS 1 and 3 were colorless. The water fraction from Reactor 2 case was colored brown/red. Peaks labelled A,B,C,D,E,F were absent from oil incubated with organisms from Reactor 2.



PANEL 1



PANEL 2



PANEL 3

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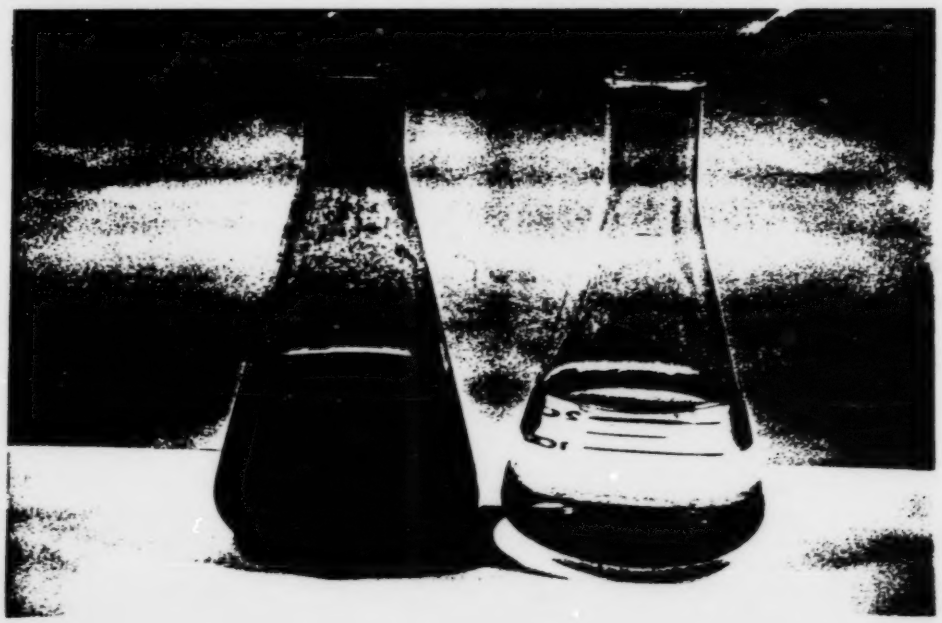
Figure 3: Growth of algal populations in water traps receiving evolved gases from reactors

PANEL A

Left: Water trap from Reactor 2; Right: Water trap from Reactor 3



PANEL B

Left: Water trap from Reactor 2; Right: Water trap from Reactor 3 three months after inoculation with the algae from Reactor 2 trap

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Figure 4: Gas chromatograms of the oil recovered from Reactor 1 over the course of the experiment

The constant peak at 50 minutes is the internal standard eicosane

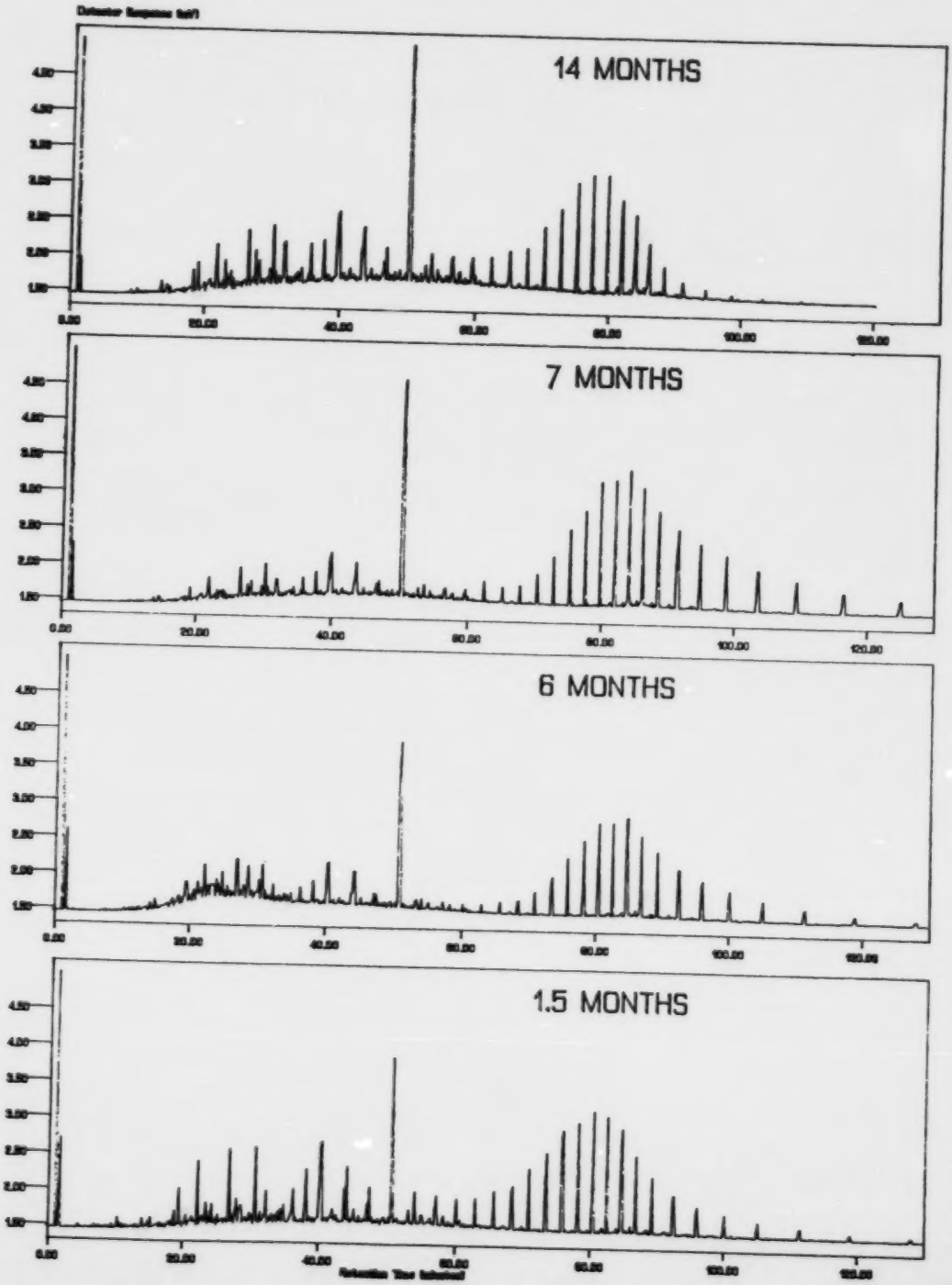

Figure 5: Gas chromatograms of the oil recovered from Reactor 2 over the course of the experiment

The constant peak at 50 minutes is the internal standard eicosane

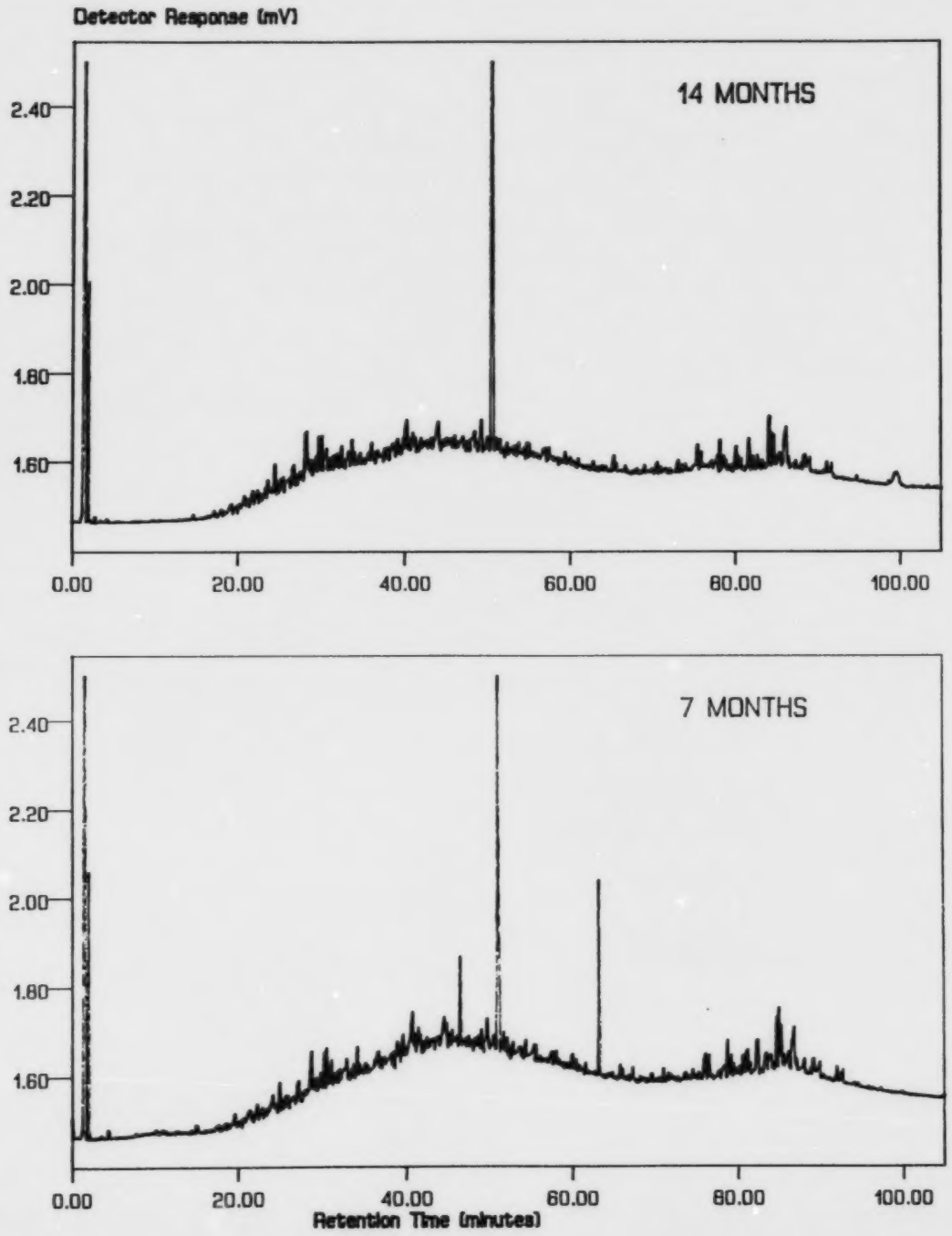

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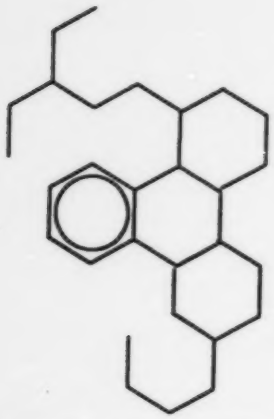
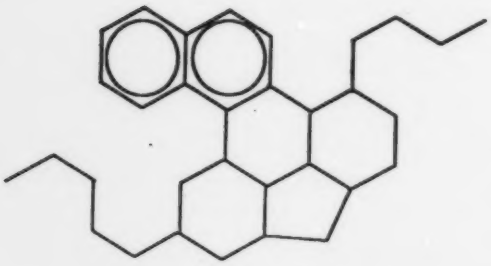
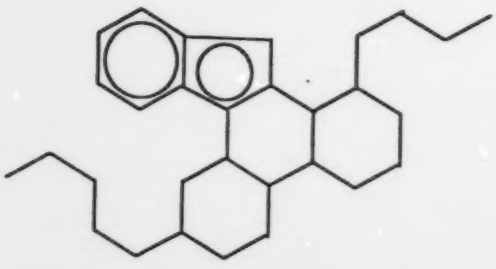
Figure 6: Average molecular structure of Alberta heavy crude (from Reference 10)



Average structure for blended crude



Average structure for native crude



Average structure for steamflood crude

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10.0 APPENDICES

APPENDIX I
THE DEAN STARK OIL EXTRACTION TECHNIQUE

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SYNCRUDE
ANALYTICAL METHODS FOR OIL SAND AND BITUMEN PROCESSING

SYNCRUDE CANADA LIMITED
EDMONTON, ALBERTA, CANADA
August 1979

Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples (Classical)

Scope: This method determines the bitumen, water and solids content of middlings and tailings samples. Preferred sample sizes range from 250 to 600 g, although the method may be modified for smaller samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap. The water is drained from the lower portion of the trap while the solvent recycles through the extraction thimble to dissolve bitumen. When the extraction is complete, the clean solids retained in the thimble are dried and weighed. A density measurement is employed to determine the bitumen content of the extract. Water is determined by difference.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at least 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The trap portion, which is approximately 25 mm in diameter and 220 mm long, has a volume of about 130 mL. The lower end is fitted with a stopcock for removal of water while the upper section has a 29/42 standard taper female joint to accommodate the condenser. The downcomer has a 103/60 standard taper male joint for connection to the kettle and is perforated with 3 mm diameter holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The neck has a minimum length of 390 mm and includes a 103/60 standard taper female joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness.
5. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solder bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If samples are less than 100 g, then the extraction apparatus described in Method 2.7 is used with the exception that the lower end of the water trap is fitted with a drain cock. Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 250 and 1000 mL, Class A.
11. Syringe — 5 mL, glass, Luer-Lok tip.
12. Disposable filter assemblies — Millipore Millex filters, 0.45 µm, 25 mm diameter, catalogue no. SLHA 025 OS.
13. Densimeter — six place densimeter with constant temperature water bath for temperature control to ±0.01°C. The water bath is operated at 20°C.
14. Balances:
    Top loading balance to ±0.01 g. 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 120°C.
16. Desiccator.
17. Reagents:
    Hydrochloric acid. A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
18. Distilled water.

Procedure:

Sample Handling

1. Insert 3 Kimwipes into each of a quantity of thimbles. Place the thimbles into 800 mL beakers and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Carefully add 0.5 mL of concentrated hydrochloric acid to the sample. Then add approximately 100 mL of toluene and stir until all the bitumen adhering to the wall of the sample container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 900 mL of toluene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with toluene to remove all the bitumen. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. The extraction is complete when the level of water in the trap is constant and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Calibration of Densimeter

6. Prepare a series of standard solutions of middlings and tailings bitumen in toluene covering the range 0.3 - 12 g/250 mL. (a)
7. Filter the standards through a 0.45 µm filter and determine the density of the solutions to six places.
8. Prepare a calibration curve by plotting the density of the standards versus the bitumen concentration in grams of bitumen per 250 mL. Calculate the slope and intercept of the plot using a linear least square regression. Coefficients of determination better than 0.999 are expected. The calibration does not have to be repeated daily, but several points on the calibration curve should be checked periodically to confirm the calibration.

Bitumen Determination

9. Disassemble the extraction apparatus and pour the bitumen/toluene extract into a 1000 mL volumetric flask and dilute to volume with toluene. Filter several milliliters of the solution through a 0.45 µm filter and determine its density to six decimal places. Ensure that the measured density falls within the range of the calibration.

Solids Determination

10. Remove the thimble from the extraction apparatus, place it in its beaker and dry for 12 hours at 120°C. Cool and reweigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g

S = weight of solids recovered in thimble, g

$$B = \frac{\text{Sample Density} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 4$$

= weight of bitumen in sample, g

Precision: Data tabulated below indicates typical precision values associated with the bitumen water and solids analysis of middlings and tailings samples. Estimates reflecting th repeatability of a middlings analysis were determined on 37 replicate subsample prepared by Method 1.6 and analyzed using the small extractor assemblies. Precisio values for primary and secondary tailings were evaluated from 10 replicate sample obtained in rapid succession from pilot plant process streams and analyzed using larg extractor assemblies. All data includes errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Middlings			
Bitumen	7.32	±0.15	2.05%
Water	75.91	±0.42	0.55%
Solids	16.77	±0.38	2.27%
Primary Tailings			
Bitumen	0.87	±0.06	6.90%
Water	35.01	±1.47	4.20%
Solids	64.12	±1.48	2.31%
Secondary Tailings			
Bitumen	0.44	±0.02	4.55%
Water	79.98	±1.71	2.14%
Solids	19.58	±1.71	8.73%

Comments:

a. The bitumen for the standard solutions is prepared by extracting a large numb of middlings and tailings samples on a solids extraction apparatus, removi non-filtered solids by centrifuging, removing toluene by evaporation, a determining the residual toluene content by the procedure described in Meth 2.7.

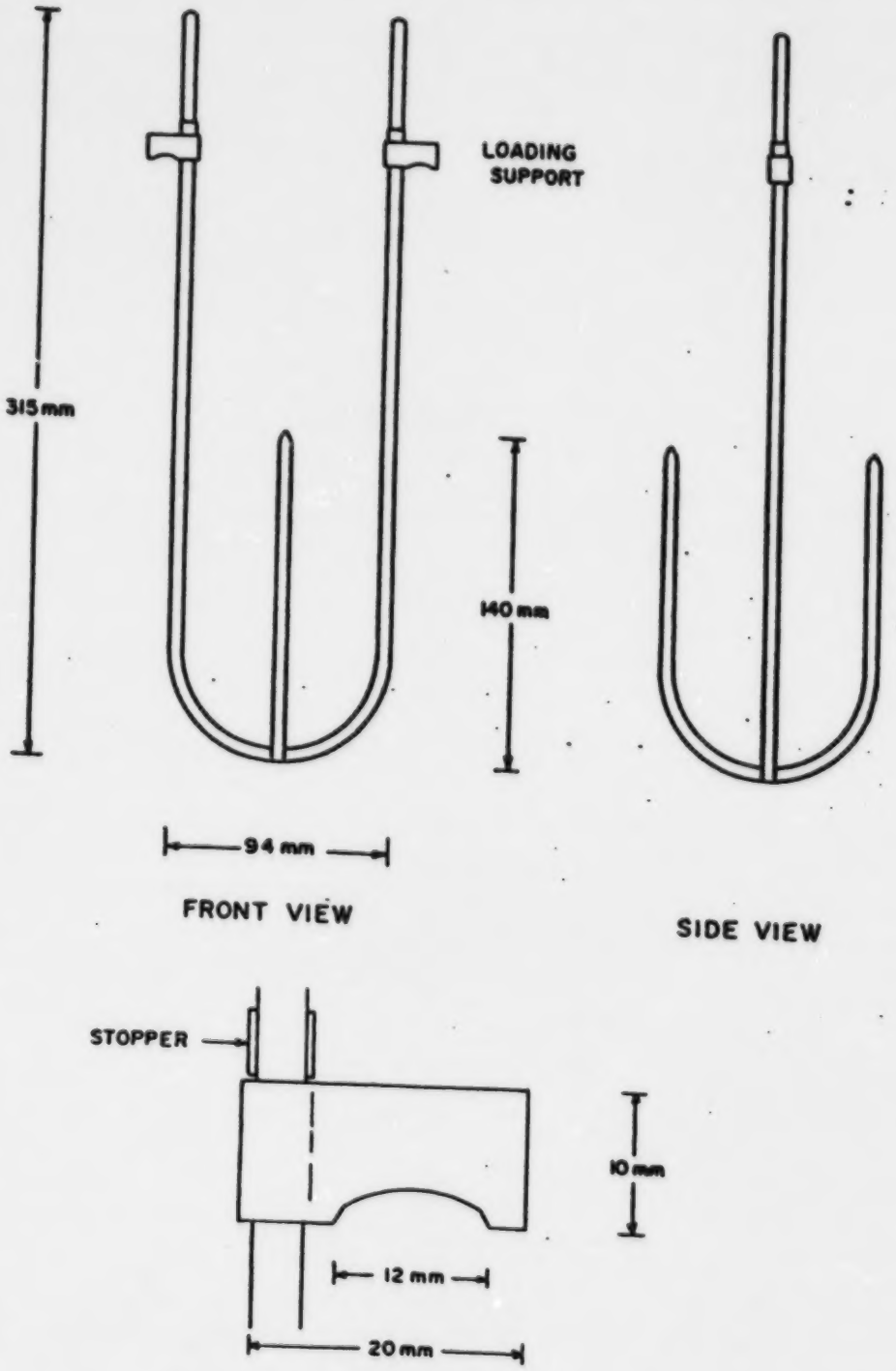

FIGURE 1: EXTRACTION THIMBLE BASKET

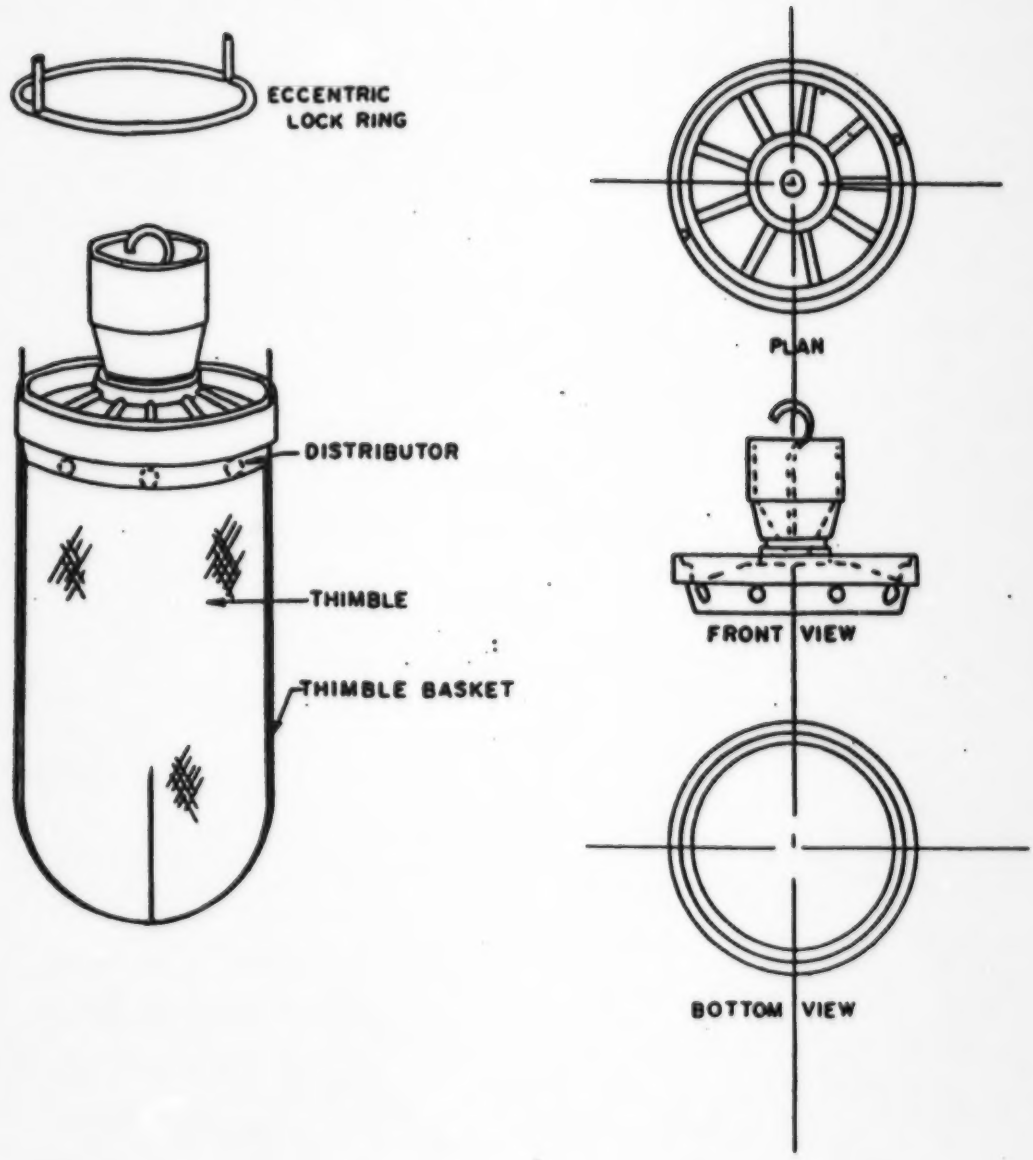

FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

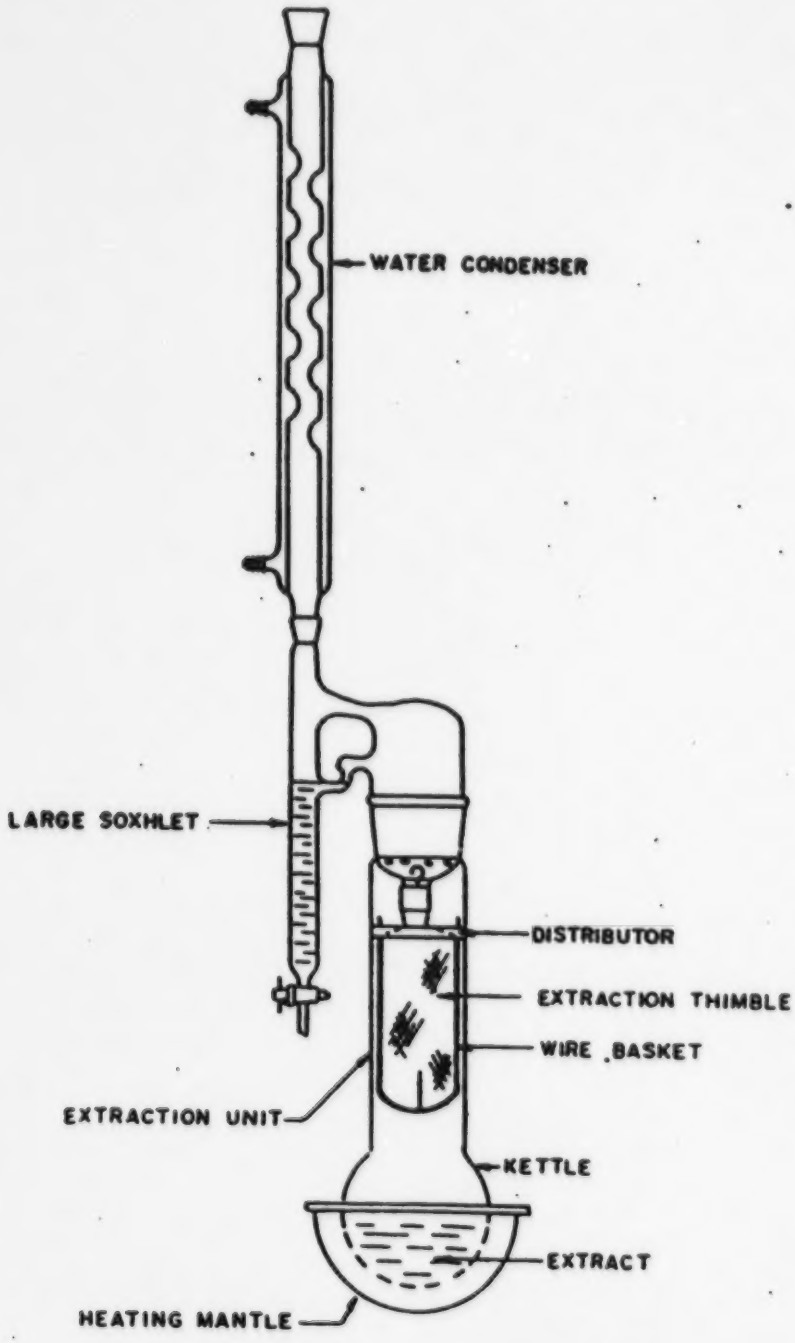

FIGURE 3: EXTRACTION APPARATUS

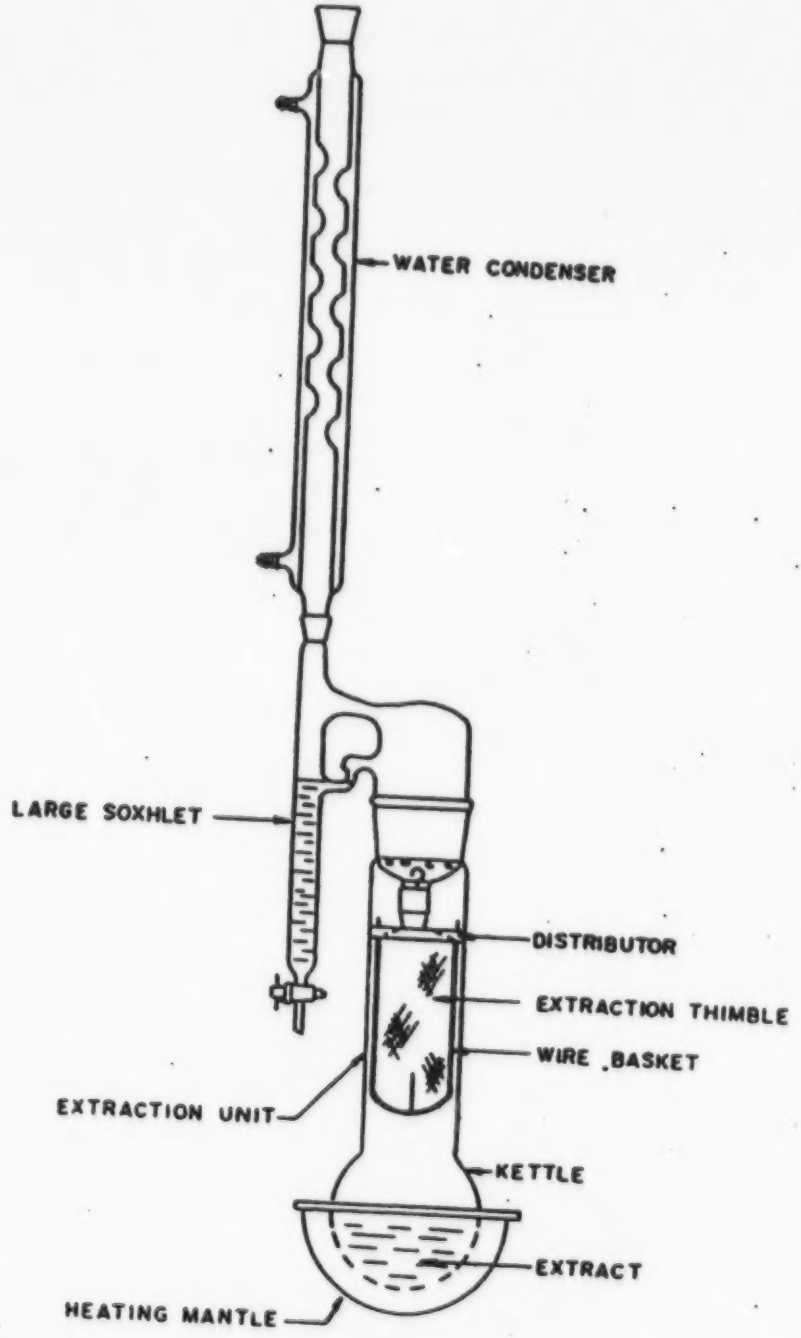

FIGURE 3: EXTRACTION APPARATUS